PHASE COMPOSITION OF THE PRODUCTS OF NITRIDING FERROSILICON WITH ZIRCON CONCENTRATE ADDITIVES

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The process of nitride formation during combustion of iron silicon with the addition of zircon concentrate in nitrogen gas is investigated. It is determined that in the presence of zircon (5 – 70%) ferrosilicon burns in a surface regime, and the products of combustion are multiphase. For the optimal parameters of synthesis (nitrogen pressure 4 – 7 MPa and sample diameter 35 – 40 mm) the products of combustion are a composition consisting of a ceramic constituent ($Si_3N_4 – ZrO_2 – Si_2N_2O$) and iron ($\alpha$-Fe). The method of acidic enrichment is used to obtain a composite ceramic powder with iron mass content 0.5%

In the last few years there has been decided interest in multiphase composition ceramic materials based on silicon nitride — $Si_3N_4 – BN$, $Si_3N_4 – SiC$, and $Si_3N_4 – TiN$. Using such materials it is possible to obtain finished articles with improved properties that cannot be obtained for single-phase materials.

It has been established that to increase the heat resistance and mechanical strength of nitride-silica materials a ready zirconium dioxide powder (USSR Patents Nos. 381650 and 392048) is added to the silicon nitride powder.

Quite many methods for obtaining silicon nitride and zirconium dioxide have now been developed. However, the existing methods are characterized by high energy intensiveness, long production times, a multistage nature of the synthesis process, and the use of expensive reagents. The method of self-propagating high-temperature synthesis (SHS) is being increasingly used in practice to synthesize various inorganic compounds. The main advantages of SHS are the development of high synthesis temperatures as a result of the release of heat by the reacting system and higher rates of transformation of the initial reagents into the final products.

We have shown [2] that it is in principle possible to obtain a composite ceramic powder based on zirconium nitride and dioxide in the SHS regime. The initial reagents were the natural mineral zircon and commercial ferrosilicon, which makes it possible to lower the cost and decrease the time required to synthesize the composition $Si_3N_4 + ZrO_2$. The present article presents the results of an investigation of the effect of the basic parameters of synthesis (nitrogen pressure, sample diameter, batch composition) on the phase composition of the composite ceramic powder.

Ferrosilicon was used as the nitride-forming component of the batch instead of expensive silicon, and zircon concentrate served as the raw material for obtaining zirconium dioxide. PUD-75 ferrosilicon is process dust formed when commercial ferrosilicon is pulverized. The initial ferrosilicon consists of silicon and iron disilicide $FeSi_2$. The silicon content is 82.0%.[2] Zircon concentrate is a grainy material with the natural graininess containing more than 94% of the main mineral zircon $ZrSiO_4$. The content of zirconium dioxide in zircon concentrate from the Tugan deposit is 63.15%, and the rest of the concentrate consists of silicon dioxide and impurity (TU U 14-10-015–98).

The initial ferrosilicon and zirconium concentrate powders were dried, before nitriding, at 150 – 200°C to remove moisture and volatile impurities. To prepare the batch ferrosilicon + zircon, the individual components were mixed in the ratios indicated in Table 1. Next, the batch was poured into a gas-permeable tube and burned in a constant-pressure apparatus in a nitrogen atmosphere. A combustion wave was initiated from the igniting powder mixture using a tungsten coil, through which electric current was passed. After passage of a combustion wave, the sample was held in the nitrogen atmosphere up to complete cooling, after which the pressure was removed and the cooled product of synthesis was extracted from the apparatus for further investigations.

X-ray phase analysis of the products of synthesis was conducted using a DRON-2 diffractometer (Co radiation).

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[2] Here and below — the mass content.
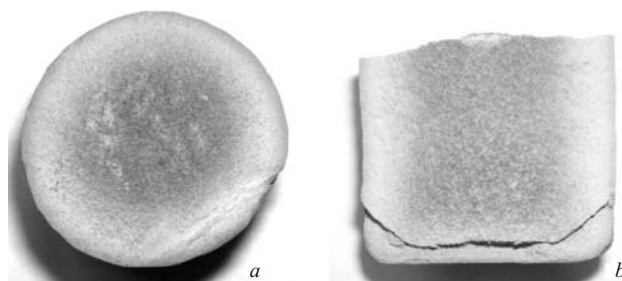
Fig. 1. Transverse (*a*) and longitudinal (*b*) sections of a sample which combusted in the surface regime.

The combustion of ferrosilicon in nitrogen gas follows the scheme

$$Si + FeSi_2 + N_2 \rightarrow Si_3N_4 + Fe + FeSi + Fe_5Si_3 + Fe_3Si.$$
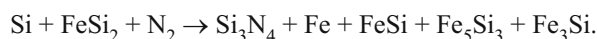
The maximum degree of nitriding is obtained when synthesis is conducted under optimal conditions (dilution with the final product, introduction of salt additives). The products of combustion contain only silicon nitride and iron:

$$Si + FeSi_2 + N_2 \rightarrow Si_3N_4 + Fe.$$
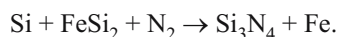
The experiments showed that combustion of ferrosilicon in the presence of zirconium concentrate (5 – 70%) occurs in a surface regime. The reaction proceeds mainly in the surface layers of the sample, as is indicated by the structural nonuniformity of the product of combustion (Fig. 1). The sample possesses a "border" with a lighter color (edge of the sample) and a central part with a darker color. X-ray phase analysis of the products of nitriding established that the central part of the sample (see Fig. 1, dark region) contains iron silicides together with silicon nitride β-Si$_3$N$_4$ and zirconium dioxide ZrO$_2$ (monoclinic and tetragonal modifications), which indicates a low degree of nitriding of ferrosilicon (in the case of complete nitriding of ferrosilicon the products of combustion consisted of silicon nitride and iron and did not contain iron silicides). The light-colored surface layer contains, besides iron silicides, α-Fe, indicating a higher degree of nitriding of the surface layer.

TABLE 1.

| Composition	Mass content, %	
	ferrosilicon	zircon concentrate
1	95	5
2	90	10
3	80	20
4	70	30
5	60	40
6	50	50
7	40	60
8	30	70
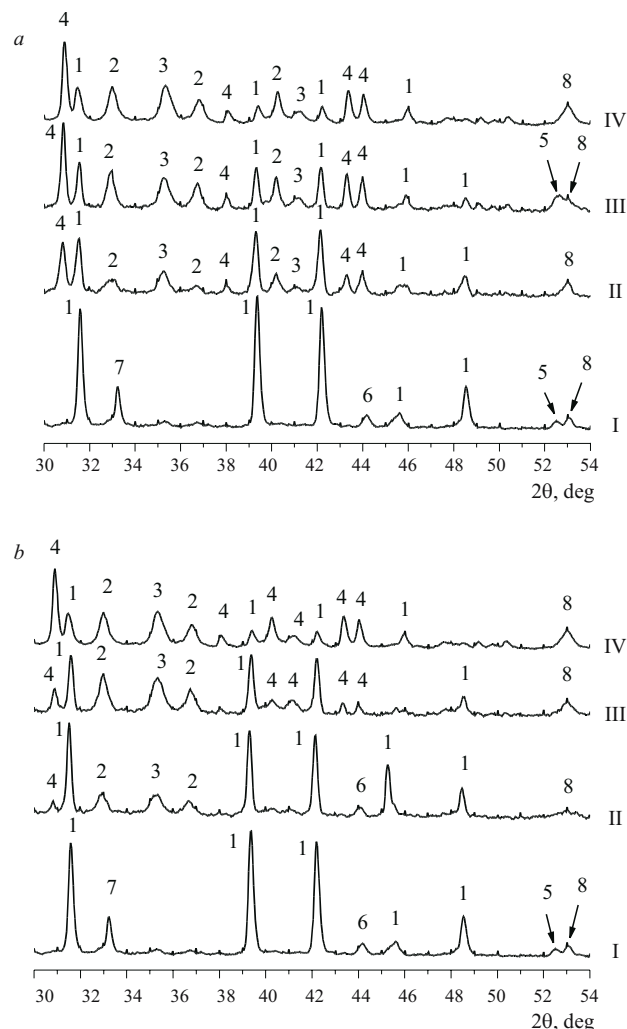
Fig. 2. Phase composition of the products of combustion versus the dilution of ferrosilicon by zircon, edge (*a*) and central (*b*) parts of the sample. Addition of zircon (%): I) 10, II) 30, III) 50, IV) 60; 1) β-Si$_3$N$_4$; 2) ZrO$_2$ (M); 3) ZrO$_2$ (T); 4) Si$_2$N$_2$O; 5) α-Fe; 6) FeSi$_2$; 7) Si; 8) FeSi.

X-ray phase analysis of the combustion products (Fig. 2) showed that their phase composition depends on the amount of zirconium concentrate added. As the amount of the additive increases, the zirconium dioxide content increases in a regular manner and the content of silicon nitride decreases. The ratio of the monoclinic (M) and tetragonal (T) phases of zirconium dioxide remains approximately the same irrespective of the amount of additive introduced. In the presence of zirconium concentrate, the interaction of ferrosilicon with nitrogen is accompanied by the formation of only the high temperature β-modification of silicon nitride. This could indicate that the nitriding process occurs at a temperature above 1500°C, since the phase transition of the low-temperature α-modification of silicon nitride into β-Si$_3$N$_4$ occurs, as a rule, at 1450 – 1500°C.
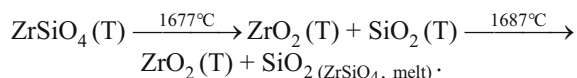
It should be noted that adding zircon concentrate results in the formation of a silicon oxynitride phase Si$_2$N$_2$O, whose
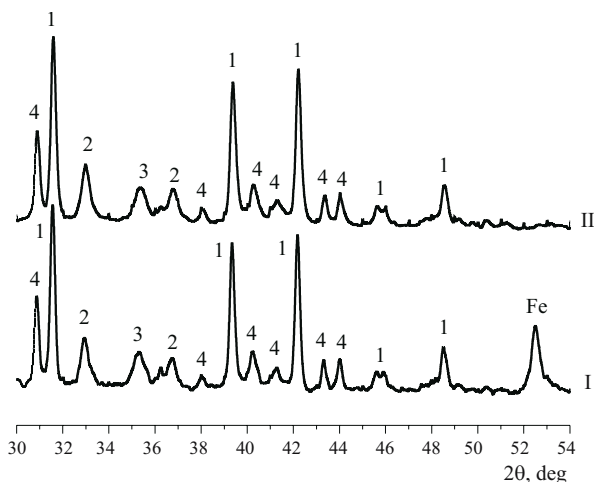
Fig. 3. Fragments of x-ray diffraction patterns of the product of combustion of a batch with the composition 40% ferrosilicon + 30% zircon + 30% nitrided ferrosilicon (nitrogen pressure 4 MPa, sample diameter 40 mm): I) before acidic enrichment; II) after acidic enrichment; 1) β-Si_3N_4; 2) ZrO_2(M); 3) ZrO_2 (T); 4) Si_2N_2O.

content in the central and outer parts of the sample is different. In the outer layer, the reflections of silicon oxynitride already appear with the addition of 10% zircon, while in the central part Si_2N_2O reflections are recorded only with 30% zircon concentrate introduced. This can be explained as follows. When temperatures above 1677°C are reached in the reaction wave of combustion, the zircon dissociates according to a solid-phase mechanism, according to the phase diagram of [3], into its component oxides: zirconium dioxide ZrO_2 and cristobalite SiO_2. A eutectic melt with the composition 5% ZrO_2 + 95% SiO_2 forms at 1687°C.

The high-temperature transformations of zircon at 1677 – 1687°C can be represented by the following scheme:

$$ZrSiO_4\,(T) \xrightarrow{1677°C} ZrO_2\,(T) + SiO_2\,(T) \xrightarrow{1687°C}$$
$$ZrO_2\,(T) + SiO_{2\,(ZrSiO_4,\ melt)} \cdot$$

High-silica zircon-silicate melt, interacting with iron silicon melt according to the scheme

$$SiO_{2\,(ZrSiO_4,\ melt)} + Si_{(Fe-Si,\ melt)} \to SiO\ (gas),$$
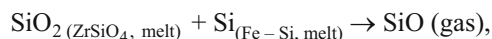
forms silicon mono-oxide gas, which nitrides in the gas phase and condenses in the colder (outer) part of the sample. The flow of silicon mono-oxide from the center to the outer layer of the sample is found to be "counter" to the nitrogen flow, which is absorbed by the combustion front from the volume of the constant-pressure apparatus and is directed toward the center of the sample. The "counterflow" resists the flow of the reacting gas, which is probably why the reaction is localized predominantly in the outer layers of the sample and a surface regime of combustion is realized.

To obtain products of combustion with a more uniform distribution of the phases and to decrease the influence of the

surface regime of combustion, it is necessary, as recommended in [4], to decrease the diameter of the sample, increase the nitrogen pressure, and increase the filtration coefficient of the reacting gas. Changing the nitrogen pressure from 3 to 7 MPa and the diameter of the sample from 60 to 35 mm results in a more uniform distribution of the phases over the cross-section of the sample, although the outer layers are once again enriched with silicon oxynitride. In addition, the products of synthesis at the center of the sample and in the surface layers contain iron monosilicide FeSi, indicating incomplete transformation of silicon into silicate nitride [5].

To increase the degree of nitriding, pre-nitrided ferrosilicon (degree of nitriding 0.76) was introduced into the initial batch (ferrosilicon + zircon). This decreases the influence of melting of the initial alloy and, as a consequence, eliminates filtration difficulties in delivering nitrogen into the reaction zone. X-ray phase analysis (Fig. 3, x-ray diffraction pattern I) shows that when the indicated additive is introduced into the initial batch more complete nitriding is attained and the products of combustion consist of a ceramic composition (Si_3N_4, ZrO_2, Si_2N_2O) and iron (α-Fe).

Acidic enrichment was used to remove iron. In the process of acidic enrichment of the products of nitriding, the iron dissolved in hydrochloric acid passes into solution and the main phases remain in the form of a dispersed residue. X-ray phase analysis (Fig. 3, x-ray diffraction pattern II) confirms that iron (α-Fe) is removed in this process. Chemical analysis showed that the content of the remaining iron in the power of ceramic composition does not exceed 0.5%.

In summary, synthesis of the composition $Si_3N_4 - ZrO_2 - Si_2N_2O$ + Fe in the system ferrosilicon + zircon is possible if pre-nitrided ferrosilicon is added into the initial batch, the nitrogen pressure is 4 – 7 MPa, and the sample diameter is 35 – 40 mm. The method of acidic enrichment makes it possible to obtain a composite ceramic powder with residual iron content 0.5%.

REFERENCES

1. N. V. Zhuravleva and E. S. Lukin, "Ceramic based on silicate nitride," *Ogneupory*, No. 1, 6 – 11 (1993).
2. O. G. Vitushkina, L. N. Chukhlomina, N. N. Golobokov, and Yu. M. Maksimov, "Obtaining composite ceramic powder based on silicate nitride and zirconium dioxide by the SHS method," in: *Proceedings of the 4th International Symposium on Combustion and Plasma Chemistry* [in Russian], Alma-Ata (2007), pp. 162 – 163.
3. N. A. Toropov, V. P. Barzakovskii, V. V. Lapin, and N. N. Kurtseva, *Phase Diagrams of Silicate Systems* [in Russian], Nauka, Leningrad (1969), pp. 104 – 106.
4. A. G. Merzhanov, *Combustion Processes and Synthesis of Materials* [in Russian], ISMAN, Chernogolovka (1998).
5. L. N. Chukhlomina, Yu. M. Maksimov, V. D. Kitler, and O. G. Vitushkina, "On the mechanism and laws of nitriding ferrosilicon in the combustion regime," *Fiz. Goreniya Vzryva*, **42**(3), 71 – 78 (2006).